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RADICAL CHAIN HALOGENATION REACTIONS
OF CHLORINE MONOXIDE

by



NESTOR NYCHKA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, RADICAL CHAIN HALOGENATION REACTIONS OF CHLORINE MONOXIDE submitted by NESTOR NYCHKA in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

The reaction of carbon tetrachloride solutions of chlorine monoxide with saturated substrates has been shown to be a free-radical chain halogenation with the over-all stoichiometry $2RH + Cl_2O \rightarrow H_2O + 2RCl$. The mechanism of the reaction was shown to involve a mixed chain with $\cdot OCl$ and $Cl\cdot$ (and/or $\cdot OH$) as the chain carrying species. The over-all reactivity and selectivity of the reagent has been shown to be similar to that displayed by t-butyl hypochlorite.

With cyclohexene, chlorine monoxide reacts spontaneously in the dark at -20° . The induced chlorination of cyclohexane under these conditions indicates that the reaction is initiated by a "molecule-induced homolysis" which exhibits a dependence on olefin concentration.

Besides water, four chlorinated compounds have been identified as the major products of the reaction of cyclohexene with chlorine monoxide in carbon tetrachloride. These four major products account for about eighty-five per cent of the available chlorine and have been identified as 3-chlorocyclohexene (I), trans-2-chlorocyclohexanol (II), trans-1,2-dichlorocyclohexane (III), and 2,2'-dichloro-cyclohexyl ether (IV). A variety of minor products make up the material balance. Two of the minor products were

identified as 4-chlorocyclohexene (V) and 2-chlorocyclohexanone (VI) and three of the products were believed to be 1-chlorocyclohexene (VII), 2-cyclohexene-1-one (VIII), and 2-cyclohexene-1-ol (IX).

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INTRODUCTION

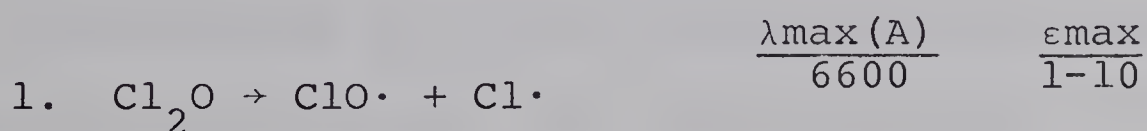
The monoxides of fluorine, chlorine, and bromine are the only known monoxides of the Group VII elements. Of these halo oxides, chlorine monoxide is the one most encountered in the literature. Much has been written about the chemistry of chlorine monoxide (1), but its use as an organic chlorinating agent has only been sparingly investigated.

Chemistry of chlorine monoxide

The compound Cl_2O is properly termed as dichlorine monoxide, but the name chlorine monoxide is retained because of its widespread usage in chemical literature. Chlorine monoxide is formally the anhydride of hypochlorous acid and exists as a yellowish red gas at room temperature (b.p. 2°). Chlorine monoxide reacts with water to give hypochlorous acid: $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HOCl}$. The equilibrium is supported by the fact that when an aqueous solution of the acid is shaken with carbon tetrachloride, the latter becomes brown-yellow and contains dissolved chlorine monoxide. The partition between chlorine monoxide in carbon tetrachloride and hypochlorous acid in water is greater by a factor of eight (2). Pure chlorine monoxide is generally prepared in the laboratory by the reaction of molecular chlorine with dry, yellow mercuric oxide: $2\text{Cl}_2 + 2\text{HgO} \rightarrow \text{Cl}_2\text{O} + \text{HgCl}_2 \cdot \text{HgO}$. The chlorine monoxide

is removed and the mercuric oxide recovered for further use by treatment of the mercuric chloride with alkali (3).

The photochemical dissociation of chlorine monoxide results in a continuous spectrum absorbing over the range 6600A to 2200A. Featuring $\cdot\text{OCl}$ as the prominent intermediate, the spectrum exhibits two main regions (4,5):



Maxima at 5300A and 4100A represent the same dissociation at other stages of excitation.

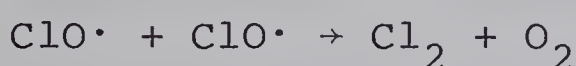
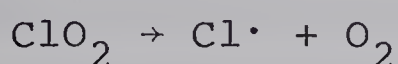
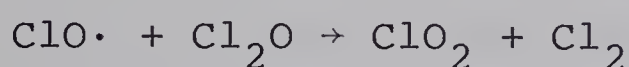
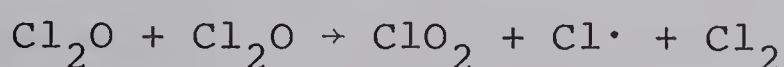


The photochemical decomposition of chlorine monoxide in carbon tetrachloride differs from that in gaseous phase (6). On the assumption that the products from the decomposition of chlorine monoxide were chlorine and oxygen, Bowen (6) found from 0.81 to 1.02 molecules of the monoxide decomposed per quantum absorbed. The gaseous photochemical decomposition of chlorine monoxide was studied by Bodenstein and Kistiakowsky (7) who concluded that two molecules of chlorine monoxide were decomposed per quantum absorbed. The small amounts of chlorine dioxide produced were considered unimportant. The smaller quantum yield in solution was attributed to the more frequent occurrence of the reactions $\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$ and $\text{Cl}\cdot + \cdot\text{OCl} \rightarrow \text{Cl}_2\text{O}$. These reactions compete with the reaction $\text{Cl}\cdot + \text{Cl}_2\text{O} \rightarrow \text{Cl}_2 + \cdot\text{OCl}$. Dickenson and Jeffreys (8) found

that the photochemical decomposition of chlorine monoxide in carbon tetrachloride is accompanied by the formation of considerable amounts of chlorine dioxide. Taking in account the amount of chlorine dioxide produced, they measured a quantum yield as high as 1.8 for the decomposition of chlorine monoxide in solution.

The mechanism by which chlorine monoxide thermally decomposes is still much of a kinetic problem. Although explosive if heated rapidly, chlorine monoxide can be thermally decomposed by careful temperature control and its rate measured by pressure changes. The rate accelerates as the reaction proceeds and the acceleration persists even in the presence of excess air, oxygen, chlorine or nitrogen. If the mechanism of thermal decomposition is a series of bimolecular reactions, then the acceleration is attributed to a series of reactions of which the first produces a pressure change less than that given by the subsequent reactions. Plotting $\log k$ against $1/T$ for each reaction results in an activation energy of 21 kcal (9). Investigation of the decomposition at various chlorine monoxide pressures shows the half-life to be dependent upon the initial concentration of chlorine monoxide (9) thereby lending evidence towards a bimolecular decomposition. The heat of dissociation as measured by sparking the gas in a calorimeter was found to be 21.7-25.1 kcals (10, 11).

These values support a chain mechanism since the energy released on bimolecular collisions would give the product molecules an energy in excess of the activation energy resulting in an immediate explosion. A complicated chain reaction, in which OCl and Cl radicals are the chain carriers, has been proposed.



The thermal decomposition of chlorine monoxide in carbon tetrachloride was found to have the same rate as in the gaseous state, so it appears that decomposition occurs by the same mechanism in both the gaseous phase and in solution (12).

The quantitative analysis of chlorine monoxide is based upon the fact that chlorine monoxide consumes acid to produce free iodine while any chlorine reacts without consuming or producing protons (3). Acid is consumed according to the equation $\text{Cl}_2\text{O} + 4\text{I}^- + 2\text{H}^+ \rightarrow 2\text{Cl}^- + \text{H}_2\text{O} + 2\text{I}_2$, while chlorine reacts in the manner $\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2$. The ratio of the titers obtained from the iodine liberated

and the acid consumed gives a measure of the purity of the chlorine monoxide (10). The unused excess of acid is determined by adding a small amount of potassium iodate and titrating with thiosulfate the iodine liberated by the reaction $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$. The concentration of chlorine monoxide and, if any, molecular chlorine is determined by:

$$\text{Cl}_2\text{O} = \frac{1}{2}(\text{moles original HCl} - \text{moles HCl left})$$

$$\text{Cl}_2 = [\frac{1}{2}(\text{total active Cl}) + \text{HCl left}] - \text{original HCl}$$

Organic reactions of chlorine monoxide

Chlorine monoxide explodes violently when in contact with organic matter, but controlled reactions of chlorine monoxide with organic compounds may be carried out in dilute carbon tetrachloride solutions. This was first reported by Goldschmidt and Schüssler (13) who stated that a carbon tetrachloride solution of chlorine monoxide reacts, often very suddenly after long standing, with saturated organic compounds, forming the same products as chlorine. The reaction of chlorine monoxide with unsaturated substrates (in carbon tetrachloride) proved to be more interesting. Addition of chlorine monoxide to olefins produced, among normal chlorinated products, the corresponding ether from the reaction of chlorine monoxide with two moles of olefin. That is, Goldschmidt and Schüssler (13) reported that chlorine monoxide reacted with trichloroethylene and

cyclohexene to give octachlorodiethyl ether and dichlorocyclohexyl ether respectively. Other products identified with certainty were pentachloroethane and chloral from trichloroethylene and 1,2-dichlorocyclohexane from cyclohexene.

In 1960, Chao and Cipriani (14) reported the chlorination of N,N-dimethylaniline with a carbon tetrachloride solution of chlorine monoxide. No details of the reaction were given; only the fact that 4-chloro-N,N-dimethylaniline was the major product. Schwabe and Gebhardt (15) reacted chlorine monoxide and benzene in carbon tetrachloride to get polychlorinated cyclohexanes, phenols, water, and oxygen.

Phillips and Shaw (16) first proposed a radical chain mechanism in the gas phase reaction of chlorine monoxide with propane. Done at 100°, the molar ratio of isopropyl chloride to n-propyl chloride was reported as constant at 7:1 up to about forty per cent decomposition of the oxide. Along with hypochlorous acid, the chlorides were the only products reported. Since the molar ratio approaches unity for molecular chlorine (17), the mechanism for the chlorine monoxide reaction is not compatible with a mechanism whose product distribution is determined by chlorine atom abstraction.

As outlined above, it is evident that controlled reactions may be carried out between organic substrates

and chlorine monoxide in carbon tetrachloride. Up until now there have been no mechanistic investigations regarding the process of reaction between organic compounds and chlorine monoxide in solution. Since chlorine monoxide exhibits a high selectivity in the gas phase (16), it is of interest that the halogenation reaction of chlorine monoxide in solution be more thoroughly understood; not only from the theoretical aspects of the reaction but also in the evaluation of chlorine monoxide as a synthetic reagent.

Part A

The Reaction of Chlorine Monoxide
with Saturated Organic Substrates

DISCUSSION AND RESULTS

Chlorine monoxide reacts with hydrocarbons in the dark slowly, but with photolysis, the reaction proceeds within minutes. Using a representative substrate, 1-chlorobutane (1.8M), and reacting it with a dilute carbon tetrachloride solution of chlorine monoxide (0.18M) resulted in the distribution of products as seen in Table I. Irradiation at 40° resulted in complete reaction in about fifteen minutes. Visually, the color of chlorine monoxide faded, and after about three minutes a cloudiness appeared and after an additional ten minutes the solution was cloudy colorless. The cloudiness was due to the production of water. Other hydrocarbon halogenations proceeded in much the same manner, only reaction times varied with various substrates. By analysis and material balance experiments the overall stoichiometry, as shown in Table I, is summarized by the equation:



Observing the effects of reaction variables is a valuable guide in determining and testing for a free radical chain mechanism (18). Stability in the dark, reactivity in the light, chemical inhibition, and chemical initiation are four characteristics of most free radical chain reactions. Table II shows the result different experimental conditions had on the reaction of 1-chlorobutane with chlorine monoxide.

The induction period was taken from the time of equilibration (at 40°) to the time a visible change occurred; that is, an appearance of a cloudiness in the ampoule. The cloudiness was due to the precipitation of water. The reaction was complete when the reaction mixture became cloudy, colorless; at which time there was no titer.

TABLE I

Products of the Photoinitiated Reaction of 1-Chlorobutane
with One Mole of Chlorine Monoxide
 (1:10 mole ratio, 40°, CCl₄)

Products	Moles of product found*
1,1-dichlorobutane	0.40 ± 0.01
1,2-dichlorobutane	0.46 ± 0.01
1,3-dichlorobutane	0.93 ± 0.02
1,4-dichlorobutane	0.18 ± 0.003
HCl	0.06 ± 0.003
H ₂ O	0.97 ± 0.003

*Reported values are average numbers from three or more independent experimental determinations.

Degassed reaction mixtures were more reactive than mixtures with atmospheric amounts of oxygen (Table II, expts. 1 and 3). The inhibition by oxygen was also apparent when the reactions were photolysed (Table II, expts. 4 and 5). Although the reaction mixture was not entirely stable in the dark, it still showed less reactivity than the

TABLE II

Reaction of 1-Chlorobutane and Chlorine Monoxide at 40°
(0.18 molar chlorine monoxide, 1.8 molar 1-chlorobutane).

Expt. ^a	Induction period (min.)	Reaction time (min.)	Conditions
1	95	900 ^b	dark, degassed
2	120	3000 ^c	dark, degassed, 0°
3	5000	--	dark, under oxygen
4	3	10	photoinitiation, degassed
5	11	70	photoinitiation, under oxygen
6	20	80	AIBN ^d , degassed
7	60	2000	AIBN ^d , under oxygen

^a Values reported are averages from three or more independent experiments.

^b Iodometric titration showed 2-3% of molecular chlorine present at reaction completion.

^c Iodometric titration showed the reaction to have proceeded about 40% in 3000 minutes.

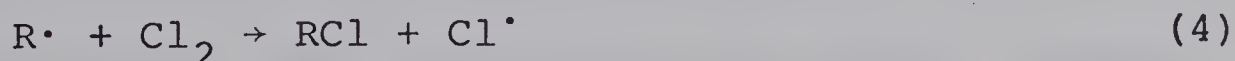
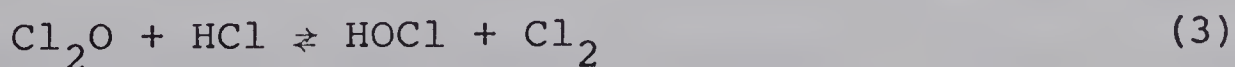
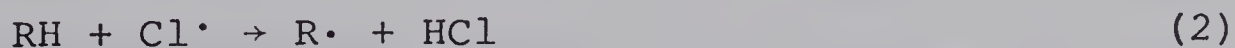
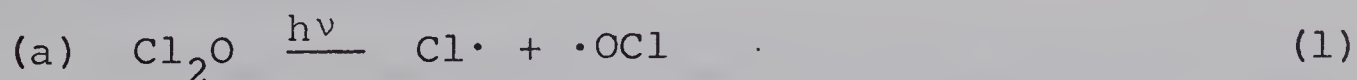
^d AIBN concentrations were 0.02 mole % of those for chlorine monoxide.

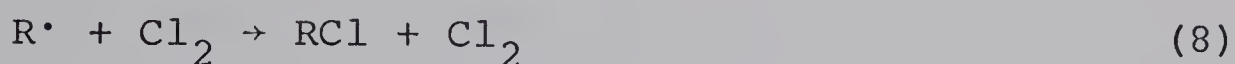
photolysed reactions. Chlorine monoxide in carbon tetrachloride is known to decompose at moderately higher temperatures (12), and since the reaction time of chlorine monoxide and 1-chlorobutane is longer at 0° (Table II, expt. 2), a slow thermal initiation best explains the "spontaneous" reaction of degassed samples in the dark (Table II, expt. 1). The initiation by trace amounts of AIBN (azobisisobutyronitrile) is a further indication that a chain reaction is occurring (Table II, expts. 6 and 7). The observations as reported in Table II sum up to indicate that a free radical chain mechanism is operating in the halogenation of 1-chlorobutane by chlorine monoxide.

Based on the product analysis after halogenation (Table I) and the results of inhibition and initiation experiments (Table II), possible chain mechanisms may now be proposed and tested for.

The first chain mechanism involves abstraction entirely by chlorine atoms. In the sequence of reactions (eq. 1-8), abstraction of hydrogen by atomic chlorine is the product determining step.

SCHEME I:

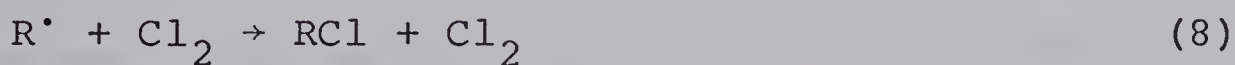
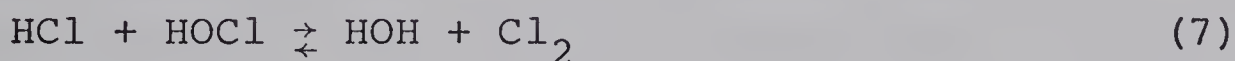
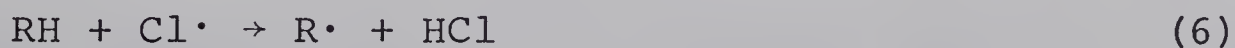
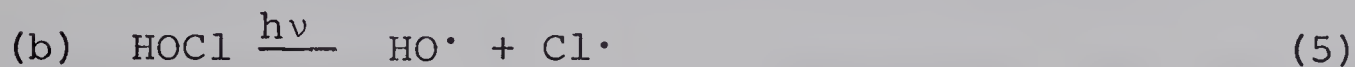
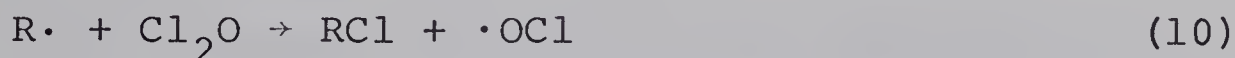
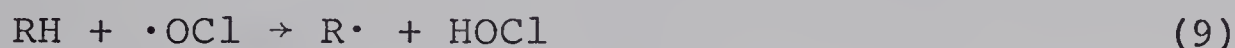
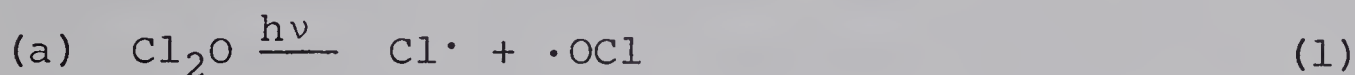




Equilibrium 7(1) which is a consequence of equilibrium 3(19), accounts for the production of water; both of these equilibria are known.

The second mechanism employs OCl radicals as an abstracting species (eq. 1, 9, 10). The hypochlorous acid produced in reaction 9 is utilized as in the first scheme

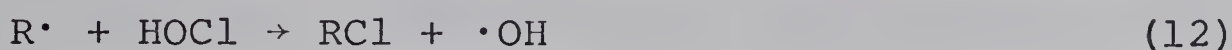
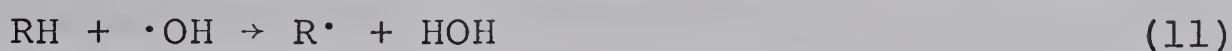
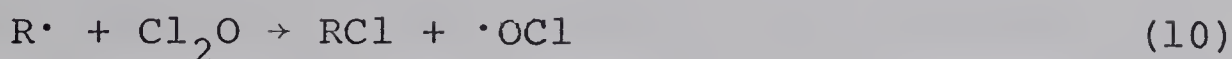
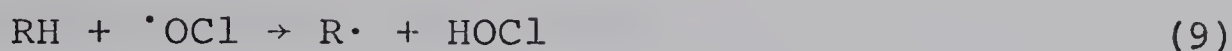
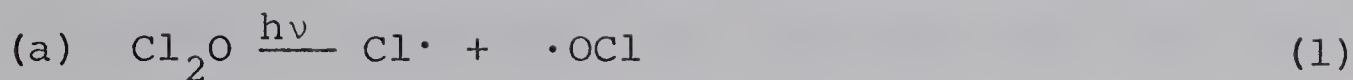
SCHEME II:



(eq. 5-8). This second mechanism results in a mixed chain involving both OCl and chlorine radicals as the product determining species.

Another mixed chain results if hypochlorous acid is consumed differently. Since the initiation step (eq. 5) produces chlorine and hydroxyl radicals, either of these radicals could react to continue the chain. Scheme II showed

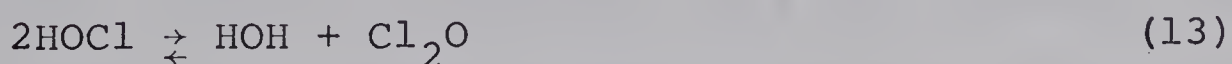
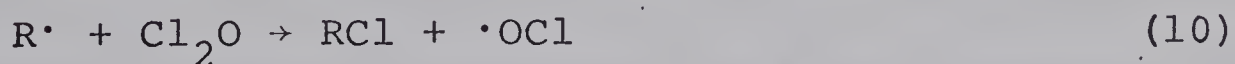
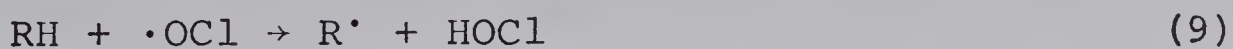
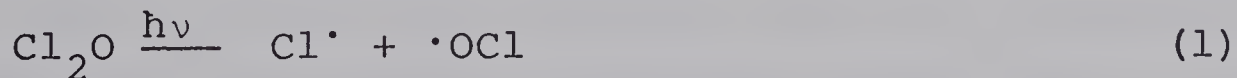
SCHEME III:



a mixed chain of OCl radicals and chlorine radicals; therefore, it follows that a mixed chain of OCl and hydroxyl radicals is possible. That is the third mechanism; the hypochlorous acid from reaction 9 reacts with substrate by hydroxyl radical abstraction.

Since chlorine monoxide is the anhydride of hypochlorous acid (1), it is conceivable that the equilibrium between hypochlorous acid and chlorine monoxide in carbon tetrachloride (2) can operate to facilitate a fourth mechanism. This scheme (eq. 1, 9, 10, 13) shows hydrogen

SCHEME IV:



abstraction performed solely by the OCl radical. The extent

to which the equilibrium 13 is occurring must depend upon the ratio of the aqueous and organic phases and their distribution coefficient (2), and also upon the rates at which the reactions take place.

As seen in the four schemes above, radicals are produced initially; then they react to form products in the propagation steps. Understanding the propagation steps is the key to understanding the nature of the products. The above sequences involve different propagation steps in which various abstracting radicals are operating. By investigation of products formed, their distribution and reactivity, conclusions may be drawn to determine the operative sequence in the chlorine monoxide halogenation.

Halogenation of negatively substituted alkanes is an invaluable method (20, 21) for investigating the selectivity and response to polar effects exhibited by the radical abstracting species. Substrates 1-chlorobutane, 1-chloropropane, and n-butyronitrile were allowed to react with chlorine monoxide and the product distribution compared with those distributions obtained from the halogenations by chlorine and t-butyl hypochlorite (Table III). It is evident that the difference in isomer distribution is sufficient enough to eliminate the first mechanism (Scheme I): that which proposes sole extraction by chlorine atoms. It is of interest to note that the reactivity of chlorine

TABLE III

Comparison of the Isomer Distributions for the
Halogenation of Substituted Alkanes with Several
Chlorinating Agents (40°, photoinitiation, CCl₄ solvent)

Molecule	Reagent	Isomer distribution %			
		1,1	1,2	1,3	1,4
1-chlorobutane	Cl ₂ O	21.6	19.0	50.8	8.6
	<u>t</u> -C ₄ H ₉ OCl ^a	21.3	19.6	43.6	15.4
	Cl ₂ (34% neat) ^b	6.6	23.5	51.4	18.4
1-chloropropane	Cl ₂ O	42.8	42.4	14.8	
	<u>t</u> -C ₄ H ₉ OCl ^a (neat)	47.7	41.4	10.9	
	Cl ₂	11.8	57.6	30.7	
<u>n</u> -butyronitrile	Cl ₂ O	--	20.1	38.9	41.0
	<u>t</u> -C ₄ H ₉ OCl ^a (neat)	--	22.4	43.7	33.9
	Cl ₂ ^c	--	0	69	31

^a C. Walling and B.B. Jacknow, J. Am. Chem. Soc., 82, 6113 (1960)

^b C. Walling and M.F. Mayahi, *ibid.*, 81, 1485 (1959).

^c A. Bruylants, M. Tits, C. Dieu, and R. Gauthier, Bull. Soc. Chim. Belges, 61, 266 (1952).

monoxide with substituted alkanes is almost identical with that of t-butyl hypochlorite. This observation is an indication that OCl radicals may be an abstracting species with a reactivity and selectivity similar to the t-butoxy radical.

The conclusion, as drawn from the isomer distribution in Table III, implies that the chain halogenation of alkanes by chlorine monoxide is propagated by a species other than the chlorine atom. In other words, the reaction of alkanes with chlorine monoxide in carbon tetrachloride is a chain halogenation in which the OCl radical is, at least in part, the product determining species. There is not, as yet, enough experimental evidence to eliminate the possibility that a mixed chain may also be operative. Table IV compares primary:secondary:tertiary hydrogen selectivity ratios that arise from the halogenation of n-butane and 2,3-dimethylbutane with various chlorinating agents. Also, the selectivity ratio of hydroxyl radicals, as reported by Bérces and Trotman-Dickenson (22), is included to complete the comparison. The reaction of hydroxyl radicals (produced in an aqueous medium) with hydrocarbon gases, a two phase reaction, shows a selectivity similar to that of chlorine in the gas phase. Therefore, under the same conditions, it seems plausible that hydroxyl radicals may have the same reactivity and

TABLE IV

Comparison of Selectivity between Chlorinating Reagents^a

Chlorinating agent ^a	Primary	Selectivity Secondary	Tertiary
Cl ₂ (25°) ^{b,c}	1	3.7	4.2
Cl ₂ (40°) ^{b,c}	1	2.8	3.9
Cl ₂ (25°) ^{d,e}	1	5.4	6.3
Cl ₂ (27°) ^f	1	3.9	5.1
HOCl (40°, aqueous) ^b	1	3.8 ± 0.3	4.6 ± 0.1 ^g
<u>t</u> -C ₄ H ₉ OCl (40°) ^{b,h}	1	12.2	44
Cl ₂ O (100°, vapor phase) ⁱ	1	21	--
Cl ₂ O ^b	1	11.5 ± 0.3	24 ± 1 ^g
Hydroxyl ^{e,j}	1	4.7	9.8

^a All are chlorinating agents, except hydroxyl radical, which was included for comparison.

^b Values obtained from halogenation of 2,3-dimethylbutane and n-butane.

^c Values for photochlorination in CCl₄: G.A. Russell, J. Am. Chem. Soc., 80, 4997 (1958).

^d Values for gas-phase photochlorination: see ref. 15.

^e These ratios are taken from relative reactivities between different molecules with ethane having a reactivity of one.

^f Values for gas-phase photochlorination: P.C. Anson, P.S. Fredericks, and J.M. Tedder, J. Chem. Soc., 918 (1959).

Footnotes to Table IV contd.

^g Errors are average deviation from the mean of three or more independent experiments.

^h See ref. 20, 27.

ⁱ See ref. 4.

^j See ref. 22.

selectivity as do chlorine atoms. The selectivity of chlorine monoxide in carbon tetrachloride is different from all the other chlorinating reagents listed in Table IV; also, the selectivity is different in the gas phase (4). Thus, in solution, the process of chlorination of hydrocarbons by chlorine monoxide appears to be a mixed chain.

If a mixed radical chain is operative, then the OCl radical is not the sole product determining species in the chlorination of hydrocarbons by chlorine monoxide in carbon tetrachloride. Therefore, a mixed chain can only result if radicals arising from hypochlorous acid take part in the chain sequence. The extent to which hypochlorous acid contributes to the chain sequence must depend on the extent to which equilibrium 13 is occurring. This equilibrium, in turn, depends upon the ratio of organic and aqueous phases and their distribution coefficient as they exist under the reaction conditions. Altering the ratio of organic and aqueous phases in the chlorine monoxide reaction would be expected to alter the concentration of hypochlorous acid present in the reaction mixture. If radicals arising from hypochlorous acid take part in the chain sequence, then a variation in hypochlorous acid concentration would be expected to influence the chain process. This influence would be reflected by a variation in the product distribution resulting from the chlorine monoxide chlorination of a substituted alkane.

Tables V and VI show how isomer distributions of substituted alkanes are affected by varied organic/aqueous phase ratios. Addition of water (sufficient enough to convert the chlorine monoxide to hypochlorous acid) to chlorine monoxide solutions of carbon tetrachloride and photolysis with continuous agitation resulted in an isomer distribution which was not altered enough from that of the reaction carried out without added water (Tables V and VI, reaction 2). The reactions of 1-chloropropane and 1-chlorobutane with hypochlorous acid in the presence of carbon tetrachloride (Table V, reactions 4 and 5; Table VI, reaction 4) exhibit a product distribution approaching that obtained from the reaction of these same hydrocarbons with chlorine (Table V, reaction 6; Table VI, reaction 5). This variation in product distribution indicates that the equilibrium between hypochlorous acid and chlorine monoxide in the presence of water and carbon tetrachloride lies only in the direction of hypochlorous acid when there is sufficient water present. Since water is produced in the reaction of chlorine monoxide with alkanes, it is reasonable to assume that radicals arising from hypochlorous acid contribute to the mixed chain mechanism.

Additional evidence in support of a mixed chain is obtained from further studies of the reaction of chlorine

TABLE V

Isomer Distribution for 1-Chloropropane Halogenations (40°, photoiniated)

Reaction	Reagent	Solvent (organic:aqueous ratio)	Isomer distribution, % ^a		
			1,1	1,2	1,3
1	Cl ₂ O	CCl ₄	42.8 ± 0.7	42.4 ± 0.3	14.8 ± 1.1
2	Cl ₂ O	CCl ₄ -H ₂ O (100:1)	42.0 ± 1.5	42.0 ± 0.9	16.0 ± 0.4
3	HOCl	CCl ₄ -H ₂ O (10:1)	21.8 ± 0.4	46.9 ± 0.3	31.3 ± 0.2
4	HOCl	CCl ₄ -H ₂ O (1:1)	17.2 ± 0.4	49.2 ± 1.1	33.6 ± 1.6
5 ^b	HOCl	C ₃ H ₇ Cl-H ₂ O (1:1)	20	50	30
6	Cl ₂	CCl ₄	11.8 ± 0.7	57.6 ± 0.5	30.7 ± 0.3

^a Values are averages of the results of three or more independent experiments;

errors are average deviations from the mean.

^b Results from single experiment only.

TABLE VI

Isomer Distribution for 1-Chlorobutane Halogenations^a (40°, photoinitiation)

Reaction	Reagent	Solvent (organic:aqueous ratio)	Isomer distribution, %			
			1,1	1,2	1,3	1,4
1	Cl ₂ O	CCl ₄	21.6 ± 0.2	19.0 ± 0.1	50.8 ± 0.3	8.6 ± 0.3
2	Cl ₂ O	CCl ₄ -H ₂ O (100:1)	17.4 ± 0.5	21.0 ± 0.4	47.0 ± 1.0	14.6 ± 0.9
3	HOCl	CCl ₄ -H ₂ O (10:1)	7.8 ± 1.6	21.7 ± 2.1	47.1 ± 2.2	23.4 ± 1.7
4	HOCl	CCl ₄ -H ₂ O (1:1)	7.0 ± 0.1	23.2 ± 0.2	43.8 ± 0.1	26.0 ± 0.2
5 ^b	Cl ₂	neat, 34°C	6.6	23.5	51.4	18.4

^a Results are average values from three or more independent experiments; errors are average of deviation from the mean.

^b Results from duplicate experiments only.

^c C. Walling and M.F. Mayahi, J. Am. Chem. Soc., 81, 1485 (1959).

monoxide with 1-chloropropane (Table VII). The reaction, analyzed in various stages of progress, shows the distribution buildup which approaches the distribution as shown for complete reaction (Table V, reaction 1). As the reaction proceeded either in the dark ("spontaneous" reaction) or by photoinitiation, the distribution changes from one indicative of the OCl radical to an isomer distribution in part determined by abstraction by atoms arising from hypochlorous acid, presumably by chlorine atom abstraction. The spontaneous reaction differs from the photoinitiated one only in the latter stages. As the reaction progresses, a buildup of hypochlorous acid occurs. Recalling the equilibrium reaction 13 and the experiments done with hypochlorous acid (Tables V and VI), it is evident that as the buildup of hypochlorous acid occurs, the equilibrium would favor the formation of chlorine monoxide (since the organic phase is in large excess). The chlorine monoxide undergoes decomposition in the dark and reacts with 1-chloropropane to give products arising from the OCl radical chain (eq. 1, 9, 10). That the dark reaction would not go to greater than 97-98% completion is evidence for the inactivity of hypochlorous acid in the dark. However, the remaining 2-3% was found to be molecular chlorine and this is presumed to be formed by the reaction of hydrochloric acid with hypochlorous acid (eq. 7).

TABLE VII

Isomer Distribution of 1-Chloropropane at Various
Stages in the Reaction with Chlorine Monoxide at 40°

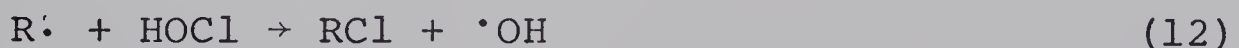
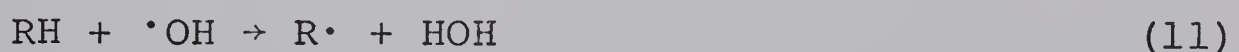
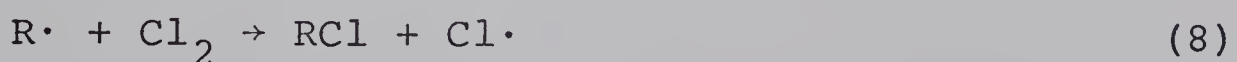
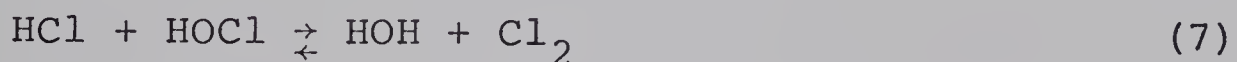
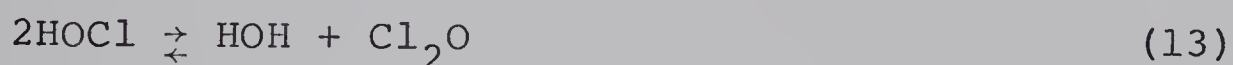
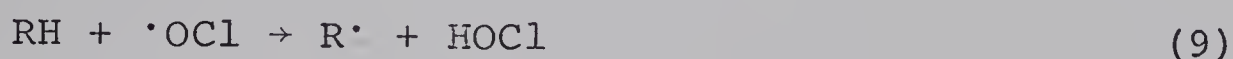
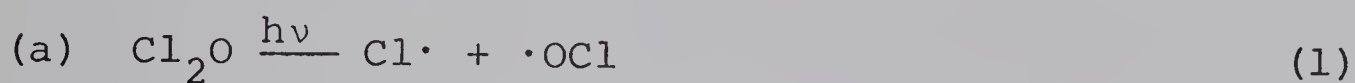
Per cent active chlorine consumed	time (min.)	Isomer distribution, %		
		1,1	1,2	1,3
25	10	60.9	33.5	5.6
32	6	60.1	33.7	6.2
35	27	60.1	33.8	6.1
49 ^a	1.5 ^b	59.1	33.9	7.0
50	90	59.2	34.4	6.4
59 ^a	23 ^c , 3 ^b	58.2	34.4	7.4
62 ^a	5 ^b	56.8	35.2	8.0
89	663	56.8	35.6	7.6
96	714	51.8	36.5	11.7
97	1200	50.7	36.9	11.4
98	5522	51.8	37.1	11.1
100 ^a	8 ^b	42.8	42.4	14.8

^a Reactions initiated by photolysis after equilibrium at 40° in the dark.

^b Times indicating the photolysis time after 8-min. equilibration in the dark at 40°.

^c After 23 min, this ampoule was slightly cloudy, then it was photolysed for 3 min., the reaction was quenched by potassium iodide solution, and then the ampoule analyzed.

The experiments put forth in Tables I-VII show that the proposed mechanism involving only OCl radical abstraction is definitely not the product-determining sequence of reactions, but that a mixed chain in which OCl radicals from chlorine monoxide and chlorine (and/or hydroxyl) radicals from hypochlorous acid are the chain propagating species, operates. The scheme could be a combination of some of the mechanisms proposed, that is:



There is no doubt that equations 1, 9, and 10 occur and equation 13 operates to some extent - mainly in the dark; but the problem exists whether hypochlorous acid is used up as the chlorine chain (eq. 5-8), or as the hydroxyl radical chain (eq. 5, 11, 12). Since the selectivities of chlorine atoms and hydroxyl radicals are

similar (Table IV), there is no experimental evidence favoring sequence (b) over sequence (c) or any reason for excluding contributions from both chains. More research must be done to determine the reactivity of hypochlorous acid and hence the chain mechanism of hypochlorous acid chlorinations.

EXPERIMENTAL

Materials

The preparation of chlorine monoxide, as described by Cady (3), was carried out by treating a carbon tetrachloride solution of chlorine (dried by bubbling through concentrated sulfuric acid) with excess dry, yellow mercuric oxide (B.D.H. Ltd. or Fisher Scientific Co., reagent grade). The resulting reddish brown solution, approximately 0.18M in chlorine monoxide, was filtered through a sintered glass funnel and stored in the dark, under refrigeration, in a glass stoppered bottle. At -15° the chlorine monoxide solution maintained one hundred per cent purity for at least one month. Recovery of mercuric oxide was achieved by washing the residue with a cold solution of sodium hydroxide (3).

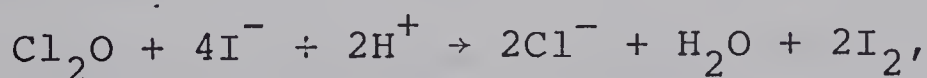
Hypochlorous acid was prepared by shaking chlorine monoxide with water and extracting the aqueous layer (3). Analysis by ultraviolet spectroscopy showed the acid to be free from detectable amounts of chlorine monoxide (see below), whereas iodometric titration determined the absence of molecular chlorine (3).

Commercially available 1-chlorobutane was distilled, and its purity was checked by boiling point, refractive index, and gas chromatography (glpc). Phillips research grade n-butane and 2,3-dimethylbutane were used without

further purification. The carbon tetrachloride (Fisher A.R. grade), used as solvent, was distilled from phosphoric pentoxide, after which the purity was checked by glpc. All other substrates were commercially available materials whose purity was checked by glpc and used as obtained.

Qualitative analysis of chlorine monoxide

The purity of chlorine monoxide was determined by iodometric titration (3). The analysis is based upon the fact that chlorine monoxide consumes acid to produce free iodine while any chlorine reacts without consuming or producing protons. Experimentally, a two milliliter aliquot of the chlorine monoxide solution was introduced into an aqueous potassium iodide (excess) solution, acidified with a known amount of excess standard hydrochloric acid (0.1M), titrating the iodine liberated with standard sodium thiosulfate solution (0.1M) and then adding potassium iodate and iodometrically titrating the acid left over. Acid is consumed according to the equation



while chlorine reacts in the manner:



Therefore, the concentration of chlorine monoxide and, if any, molecular chlorine is determined by:

$$\text{Cl}_2\text{O} = \frac{1}{4} (\text{mmoles original HCl} - \text{mmoles HCl left})$$

$$\text{Cl}_2 = \frac{1}{2} (\text{total titer} - \text{original HCl}) \quad \text{or}$$

$$\text{Cl}_2 = \frac{1}{2} \left\{ \left[\frac{1}{2} (\text{total active Cl}) + \text{HCl left} \right] - (\text{orig. HCl}) \right\}$$

Ultraviolet spectroscopy showed the chlorine monoxide solution not to be contaminated by hypochlorous acid (1):

	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$
HOCl:	230 m μ	100
Cl ₂ O:	265 m μ	500

Experimental procedure

The chlorinations of substituted alkanes were carried out in sealed Pyrex ampoules which had been degassed by the freeze-thaw method; that is, they were frozen, degassed, let thaw, frozen and degassed again before sealing the ampoules. Experiments with oxygen were carried out in ampoules which contained atmospheric concentrations of oxygen. When irradiation was used to initiate the reaction, the light source was 2-200 watt incandescent light bulbs. All reactions were carried out in a thermostated Pyrex water bath, $40.0^\circ \pm 0.2^\circ$. The average molarities of substrate to halogenating reagent were 1.8:0.18. The ampoules containing 2.5 to 4 ml of solution were equilibrated at 40° in the dark for at least fifteen minutes, and then were subjected to light. Visual commencement of the reaction occurred when a cloudiness developed and the brown-yellow color of chlorine monoxide

gradually faded. The reaction was complete, an absence of titer (3), when the ampoules were cloudy, colorless.

The reactions of hypochlorous acid and reactions of chlorine monoxide with added water, both two phase systems, were contained in ampoules that were continually shaken during photolysis.

Product analysis

Analysis of the product mixtures was carried out by glpc using an Aerograph HY-FI Model 600-D instrument equipped with a Model 328 Temperature Program Controller. Peak areas were measured using a Model 201-B Disc integrator or by the method of peak height and half height peak widths.

Chlorination of 1-chlorobutane

Chlorinated mixtures of 1-chlorobutane were analyzed by a 10 ft/0.125 in. neopentyl glycol succinate (NPGS) column having Firebrick as the solid support. The four major product peaks were identified as the assigned isomers by direct comparison of their retention times with those of authentic commercially available samples. These isomers were eluted in the order: 1,1-, 1,2-, 1,3- and 1,4-dichlorobutanes; total retention time was about twenty-five minutes. Two minor products were eluted just before the 1,4-isomer. These peaks accounted for approximately two per cent of the total products.

The minor products are most probably products of multi-chlorination and no further work was done on them.

In the material balance experiments, all the isomer peaks were measured relative to an internal standard, "Freon 112" (tetrachlorodifluoroethane). By analyzing (glpc) standard mixtures of isomeric dichlorobutanes and "Freon 112" in which mole quantities are known, direct measures of the correlation between areas and moles were determined. That is,

$$\frac{\text{moles freon}}{\text{moles product}} = k \times \frac{\text{area freon}}{\text{area product}}.$$

Actual amounts in the reaction ampoules were calculated from calibration plots of area ratios for "Freon 112"/authentic samples versus mole ratios for "Freon 112"/authentic samples.

Besides the NPGS column, a 10 ft/0.125 in. Silicone Gum Rubber SE-30 (methyl) column was used for the analysis of products from 1-chlorobutane; the retention time was about fifteen minutes. Peaks eluted from the NPGS column were measured by an integrator, while those from the SE-30 column were measured using peak height and half height peak width measurements. The isomer distributions, using two methods for measurement, differed by less than one per cent. The products account for $98 \pm 2\%$ of the total chlorine available. The water content was determined by breaking the ampoules under methanol (titrated previously

for water) and titrating to a visual end point with commercial Karl-Fischer reagent (Fisher Scientific Co., SO-K-3) (24). The small amounts of hydrochloric acid were detected by holding moist litmus paper over the mouth of a newly opened ampoule and the amount of acid was determined by iodometric titration with standard sodium thiosulfate (3).

Chlorination of 1-chloropropane

Products from the chlorination of 1-chloropropane were analyzed by three 10 ft/0.125 in. columns: diethylene glycol succinate (DEGS), Carbowax 20M, and NPGS columns. The NPGS column proved to be the most efficient one for the analysis. Two of the three product peaks were identified by their identical retention times on the three columns with commercially available compounds. The 1,1-dichloropropane isomer was assigned by elimination since it was the only peak left unidentified on the chromatogram. A check on the assignments of the isomer peaks was made by repeating the halogenation experiments of Walling using t-butyl hypochlorite and comparing the assignments with the chlorine monoxide chlorination (20).

Chlorinations at incomplete reaction were carried out in the same manner as above. After initial reaction, dark or photoinitiated (see Table VII), the reactions were quenched in liquid nitrogen and the ampoules broken under

acidified potassium iodide and titrated for active chlorine (3). After titration, the carbon tetrachloride layer was extracted, and the organic material was analyzed by glpc as described above. Assurance that the distributions were not affected by contact of the reaction mixture with water during titration was supported by repeated extractions of the organic phase. Reanalysis of the extracts resulted in no change in isomer distribution.

The photochlorination of 1-chloropropane with molecular chlorine was carried out in the same manner as the experiments with chlorine monoxide and with the same concentrations of chlorinating agent to substrate as was used in the chlorine monoxide halogenations. The distribution differs slightly from the chlorination products of SO_2Cl_2 (at 70°) which was reported to give no 1,1-dichloropropane (25).

Chlorination of n-butyronitrile

The reaction of n-butyronitrile was analyzed by glpc using a 10 ft/0.125 in. Carbowax 20M column having Chromosorb W as the solid support. Only three product peaks were observed. These products were identified by comparison of the known distribution of products resulting from t-butyl hypochlorite reactions with n-butyronitrile (20). As a check on the assignments, the retention time of the commercially available

4-chlorobutyronitrile was compared with the assignment made from the t-butyl hypochlorite reaction. Elution order for the chlorination product was 2-, 3-, and 4-chlorobutyronitrile.

Chlorination of n-butane and 2,3-dimethylbutane

An analysis of the products from the chlorination of n-butane and 2,3-dimethylbutane was used to determine the selectivity ratios of chlorine monoxide.

Primary:secondary:tertiary selectivity ratios were calculated from a comparison of product distributions:

$$\frac{\text{primary}}{\text{secondary}} = \frac{\text{area of 1-chlorobutane}}{\text{area of 2-chlorobutane}} \times \frac{2}{3}$$

$$\frac{\text{primary}}{\text{tertiary}} = \frac{\text{area of 1-chloro-2,3-dimethylbutane}}{\text{area of 2-chloro-2,3-dimethylbutane}} \times \frac{1}{6}$$

A 10 ft/0.125 in. UCON 50 HB2000 polar on firebrick column was used to analyze n-butane chlorination products. Only two products were observed. The structure of the 1-chlorobutane was assigned to its corresponding peak (second peak) on the gas chromatogram by comparison of its retention time by glpc with that of an authentic sample. The remaining (first) peak was assigned the structure of the secondary halide.

Chlorinations of 2,3-dimethylbutane were analyzed by glpc on both NPGS and UCON polar columns. Two minor low boiling products and two major higher boiling products were

observed. One peak accounted for greater than 90% of the minor products. Depending on the column used for analysis the minor product varied from 1-25% of the total. It was believed to be 2,3-dimethyl-2-butene resulting from dehydrohalogenation of the tertiary halide during analysis. This conclusion resulted from the fact that the percentage of primary chloride remained essentially constant, independent of column used, while the tertiary chloride decreased with increasing olefin percentages. The 2,3-dimethyl-2-butene structure was assigned to its corresponding peak by the comparison of its retention time with that of an authentic sample. The major products were assigned the structures 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane, eluted in that order. The tertiary chloride was prepared by the method described by Shiner (26) and its retention time by glpc was found to be the same as that for the major isomer assigned that structure.

Part B

The Reaction of Chlorine Monoxide with Cyclohexene

INTRODUCTION

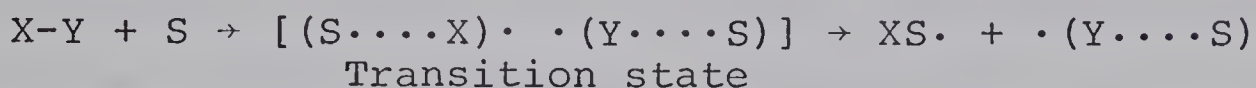
The experiments outlined in Part A have shown that chlorine monoxide in carbon tetrachloride is an efficient free radical chlorinating agent for a variety of hydrocarbons. Using light as the initiator, the reaction proceeds according to the equation



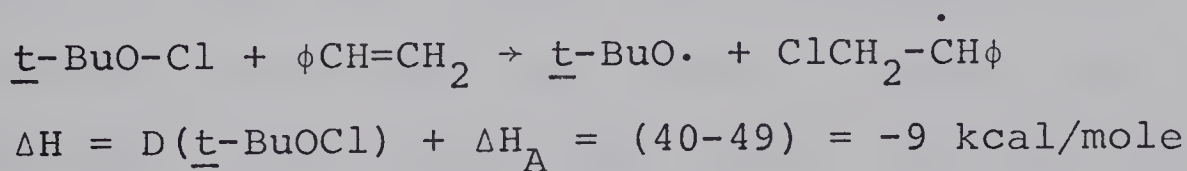
and utilizes a mixed chain sequence with $\cdot\text{OCl}$ and $\cdot\text{Cl}(\cdot\text{OH})$ as the chain carrying species. The reactivity of the combined radicals was shown to be similar to the t-butoxy radical.

A variety of olefins have been shown to react with t-butyl hypochlorite by a photoinduced radical chain process to give good yields of allylic chlorides (27). Walling, Heaton, and Tanner have observed a dark "spontaneous" reaction occurring when t-butyl hypochlorite was reacted with styrene and some acetylenes (28). The radical nature of this dark reaction is evidenced by its inhibition by oxygen, formation of radical products and by the induced chlorination of cyclohexane. The product yields of these reactions show no significant difference between light and dark reactions. The nature of the initiating process is suggested as involving the concerted breaking of the O-X bond of the hypohalite and addition of X to the π -electron system of the unsaturated molecule. A process

of this type is in agreement with a route lending to dissociation of lower overall activation energy. A general representation of this type of interaction is shown schematically as



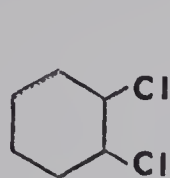
The solvent S complexes with X-Y to achieve homolysis and radical X is shown to bond to a solvent molecule. The enthalpy change in the reaction would be reduced by the bond energy of the S-X bond. If $D(\text{S-X})$ is greater than $D(\text{X-Y})$, the overall reaction will be exothermic. Consider, for example, the styrene-t-butyl hypochlorite case. The bond energy of t-butyl hypochlorite is approximately 40 kcal/mole (28), and the exothermicity of the addition of a chlorine atom to styrene is approximately 49 kcal/mole (18). Therefore, the enthalpy for the reaction involving one molecule each of t-butyl hypochlorite and styrene can be calculated.



It is clear that the molecule-induced homolysis, which is actually exothermic, will have a much lower activation energy than simple unimolecular homolysis.

Many other "dark radical" reactions are known and Poutsma cites many examples in his paper which shows that

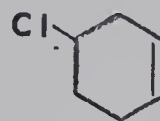
the interaction of chlorine with cyclohexene causes molecule-induced homolysis of the Cl-Cl bond (29). In cyclohexene at 25°, chlorine reacts rapidly in the absence of light and oxygen to give products (A), (B) and (C). No ionic pathway to product (C) is known; this product must arise from a radical mechanism. Products (A) and (B) are



(A)



(B)



(C)

produced by a radical process and in a concurrent ionic process. The presence of chlorine atoms has been demonstrated by the production of cyclohexyl chloride when chlorine is reacted with mixtures of cyclohexene and cyclohexane in the dark at 25°. Product (C) has been shown to depend upon the concentration of olefin. Dilution of cyclohexene with a non-olefin solvent gradually reduces the yields of the radical products and favors the formation of the ionic products (A) and (B). Since ionic chlorination of cyclohexene is at least first order in olefin, the radical process must be more than first order. Poutsma does not determine the exact kinetics but does show that a bimolecular reaction between chlorine and cyclohexene is energetically favorable over a unimolecular reaction.

The activation energy of chlorine monoxide (20-25 kcal/mole) is less than the activation energy of

t-butyl hypochlorite (40 kcal/mole) and of molecular chlorine (58 kcal/mole). The results of Part A have shown the reactivity of chlorine monoxide to be not unlike that of t-butyl hypochlorite. It is therefore of interest to determine whether chlorine monoxide reacts with unsaturated systems in a manner similar to that of t-butyl hypochlorite.

DISCUSSION AND RESULTS

Addition of a carbon tetrachloride solution of chlorine monoxide to cyclohexene (at S.T.P.) resulted in a rapid reaction; no color due to chlorine monoxide ever developed in the solution. The reactants were then degassed separately, and mixed (after temperature equilibration) by means of break seal. The reaction was still spontaneous and exothermic in the dark at -20° . Addition of atmospheric oxygen did not seem to inhibit the rate of reaction.

The above observations do not necessarily rule out a radical process, because many free radical "dark" reactions are known and Poutsma cites many examples in his paper discussing the competition between ionic and free radical reactions during the chlorination of cyclohexene (29). Walling, Heaton, and Tanner have shown that the reaction of t-butyl hypochlorite with styrene and acetylenes is spontaneous in the dark and yields addition products as well as inducing halogenation of other hydrocarbons (28). By analogy with other "dark" halogenations of unsaturated systems the investigation of a "molecule-induced homolytic decomposition" would be helpful in investigating the nature of the cyclohexene-chlorine monoxide reaction.

As mentioned previously, the radical nature of dark "spontaneous" reactions is evidenced by the induced chlorination of a saturated substrate. The influence that cyclohexene has on the reaction of chlorine monoxide with cyclohexane is shown in Table I. Under the same

TABLE I

Product Variations in the Reaction of Chlorine Monoxide with Cyclohexane in the Presence of Varied Amounts of Cyclohexene (-20°, dark, CCl₄ solvent)

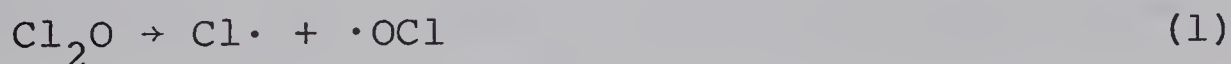
Concentration (relative amts.)			Moles chlorocyclohexane per mole Cl ₂ O ^a	
C ₆ H ₁₂	C ₆ H ₁₀	Cl ₂ O	degassed	not degassed
9.2	0.4	1.0	1.05 ± 0.02	0.40 ± 0.08
9.2	0.2	1.0	0.60	0.22
9.3	0.015	1.0	0.30 ± 0.04	0.08 ± 0.00
10.0	--	1.0	0.12 ± 0.00	0.06 ± 0.02

^a All reactions were quenched after about twenty hours at -20°. Deviations are from two or more experiments.

conditions as in Table I (dark, -20°), cyclohexane reacted with chlorine monoxide to an extent of less than ten per cent in twenty hours. Therefore, by reacting cyclohexane with chlorine monoxide in the presence of cyclohexene, the production of radicals is substantiated by an increase in the amount of chlorocyclohexane produced. From Table I,

it is evident that increasing amounts of cyclohexene produce increasing amounts of chlorocyclohexane; this therefore, implies that cyclohexene interacts with chlorine monoxide to produce radicals, which may initiate the chain chlorination of cyclohexane. The dependence of the radical reaction upon olefin concentration may also imply that the "molecule-induced homolysis" involves a kinetic order in olefin larger than unity.

The induced chlorination of cyclohexane (Table I) has shown that the reaction of chlorine monoxide with cyclohexene produces radicals. What must now be discussed is the nature of the initiating process. The simple homolytic cleavage of chlorine monoxide is implausible since similar

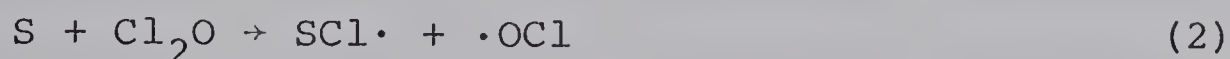


dark reactions do not occur to any appreciable extent in the presence of other easily chlorinated substrates (Part A).

The remaining alternative to initiation is a molecular "interaction" of olefin with chlorine monoxide. This form of initiation is in accordance with previously mentioned dark reactions that involved free radicals and is energetically more favorable than reaction 1 (28, 29).

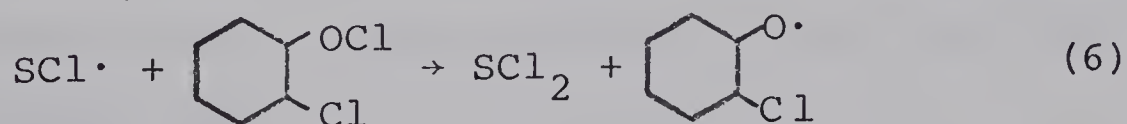
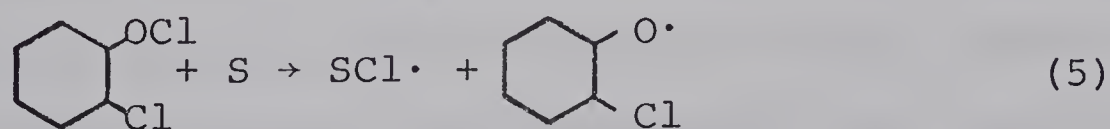
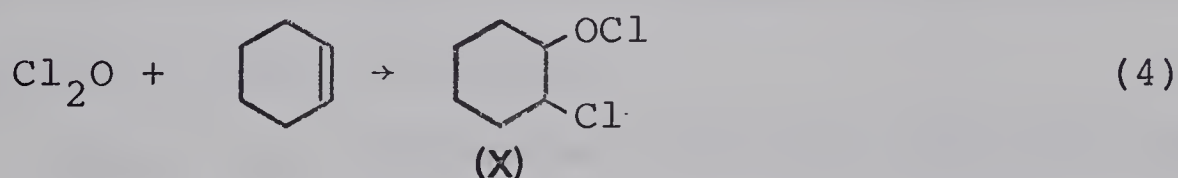
One form of molecular "interaction" is suggested schematically as equations 2 and 3.

Cyclohexene is represented in the equations as the complexing



solvent S, and SCl_2 would therefore be 1,2-dichlorocyclohexane. Whether or not production of $SCl\cdot$ is a bond forming reaction is not known, but as Walling suggests, reactions of the type shown by equation 2 are expected to be energetically favorable over interactions in which no actual bonds are formed (28).

Another form of molecular induced initiation can occur from the addition of chlorine monoxide to cyclohexene. The resulting hypochlorite (X) may "interact" with cyclohexene to initiate radicals in the manner as shown in reactions 4, 5, and 6. This form of initiation is similar to reactions 2 and 3 except that the radicals arise from a



species other than Cl_2O . In other words, initiation is based solely on the formation of 2-chlorocyclohexyl hypochlorite (X).

Secondary hypochlorites are known to be relatively unstable (30, 31) and have been reported to decompose explosively when exposed to bright light (32). However, they do not decompose spontaneously in the dark; and it is known that tertiary hypochlorites are stable in the dark in the presence of olefins (27). Nevertheless, there have been no experiments done to determine the stability of secondary hypochlorites in the presence of olefins; therefore, it is possible that spontaneous decomposition of 2-chlorocyclohexyl hypochlorite (eq. 5) could occur in the dark to give rise to radicals which could react with cyclohexene via a chain sequence involving the 2-chlorocyclohexoxy radical.

Before any conclusions were made regarding the initiation process and the ensuing radical sequence for the reaction between chlorine monoxide and cyclohexene, an investigation of the products arising from the reaction was carried out.

Analysis of the cyclohexene/chlorine monoxide reaction mixture by gas chromatography (glpc) resulted in the product distribution shown in Table II. A Karl-Fisher titration of at least three of the reaction ampoules

TABLE II

Products of the Dark Reaction of Cyclohexene

with One Mole of Chlorine Monoxide

(10:1 mole ratio, -20°, CCl₄)

Products of Reaction	Moles of product ^a	%Cl
<u>Major products</u>		
3-chlorocyclohexene (I)	0.79 ± 0.01	39.5
<u>trans</u> -2-chlorocyclohexanol (II)	0.53 ± 0.02	26.5
<u>trans</u> -1,2-dichlorocyclohexane (III)	0.082 ± 0.008	8.2
2,2'-dichlorocyclohexyl ether (IV)	0.115	11.5
<u>Minor products</u> ^b		
4-chlorocyclohexene (V)	0.026 ± 0.012	1.3
2-chlorocyclohexanone (VI)	0.027 ± 0.009	1.35
1-chlorocyclohexene (VII)	0.01	0.5
2-cyclohexene-1-one (VIII)	0.027 ± 0.007	1.35
2-cyclohexene-1-ol (IX)	0.040 ± 0.009	2.0
unidentified products	0.056	2.8- 5.6 ^c
	Total	94.5- 97.3

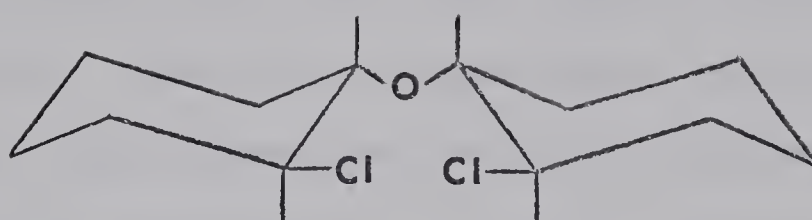
^a Reported values are average numbers from three or more independent experimental determinations, except when no deviations are shown.

^b Amounts of minor products are merely estimates. See experimental for procedure used.

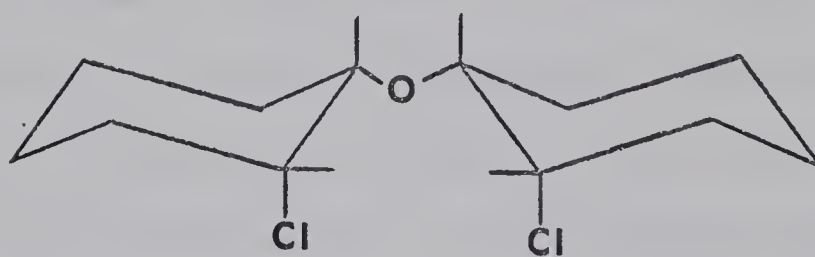
^c The unidentified products are reported as a range on the assumption they contain from one to two chlorine atoms per molecule.

(reactions carried out at room temperature) showed 0.50 ± 0.03 moles of water for every mole of chlorine monoxide. The minor products (Table II) were present in amounts large enough to detect and identify with reasonable certainty by glpc retention times, but too small to isolate or to measure very accurately. Two of the minor products were identified as 4-chlorocyclohexene (V) and 2-chlorocyclohexanone (VI). One minor product was believed to be 1-chlorocyclohexene (VII) and two other minor peaks were shown by retention time to correspond to 2-cyclohexene-1-one (VIII) and 2-cyclohexene-1-ol (IX). Small amounts of other products, designated as unidentified products in Table II, were shown by glpc to be present in the reaction mixture. Some of these unidentified products decomposed slowly at room temperature to give increasing amounts of products (VIII) and (IX). No cis-1,2-dichlorocyclohexane, cis-2-chlorocyclohexanol, cyclohexanol, cyclohexene oxide, or cyclohexane were detected as any of the products.

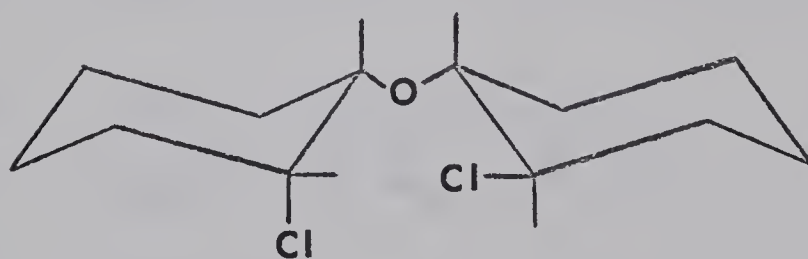
Since the dichlorocyclohexyl ether has four centers of substitution, four stereoisomers are possible:



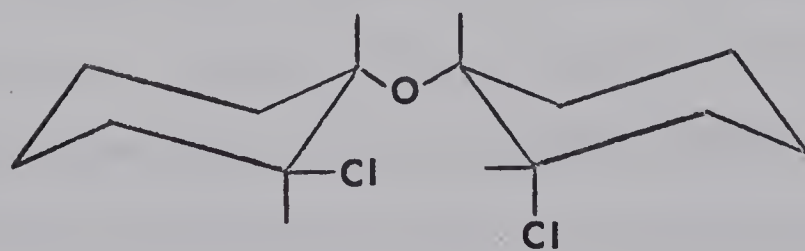
trans-trans-



cis-cis-



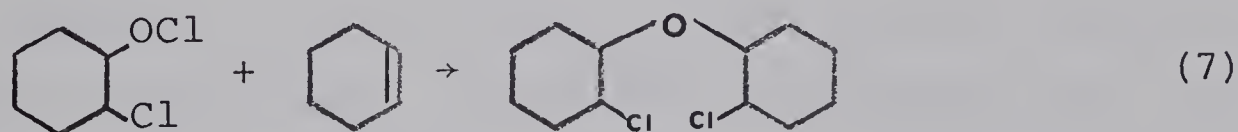
cis-trans-



trans-cis-

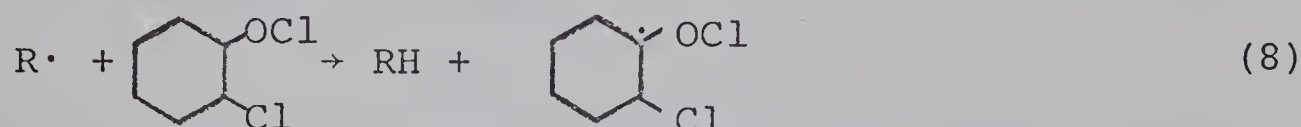
No characterization of the ether was done except that analysis by glpc showed the ether to be seventy per cent one isomer and at least two isomers made up the other thirty per cent.

Table II shows that the four major products account for the majority (86%) of the available chlorine. The production of these major products is consistent with a radical process and does not eliminate any of the initiation processes already discussed. The production of twelve per cent of the ether is supporting evidence for the presence of 2-chlorocyclohexyl hypochlorite (X). The formation of the ether can only arise from the addition of the hypochlorite to cyclohexene (reaction 7). Whether the addition is free radical or ionic is not known, but reaction 7 is not unique to hypochlorites. Free

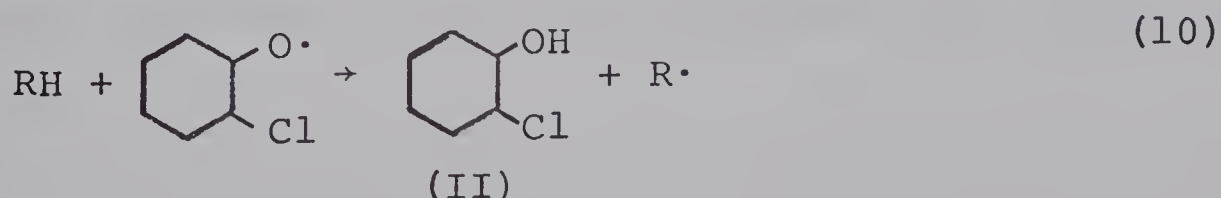


radical additon of t-butyl hypochlorite to some olefins affords up to seventeen per cent addition product (27). These reactions of olefins with t-butyl hypochlorite did not occur spontaneously but were photoinduced. However, it was previously mentioned that the reactivity of secondary hypochlorites with olefins was not known.

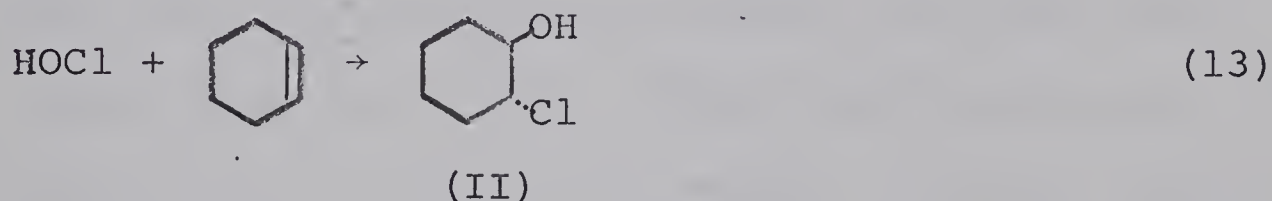
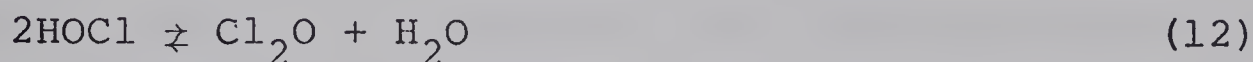
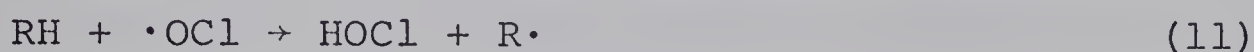
Additional supporting evidence for the formation of 2-chlorocyclohexyl hypochlorite is the identification of small amounts of 2-chlorocyclohexanone (Table II); the presence of which is consistent with the observation that carbonyl compounds are the major products in the decomposition of primary and secondary hypochlorites (30, 31, 32). These carbonyls are proposed to arise from α -hydrogen abstraction from the hypochlorite. Formation of product (VI) may be explained in the manner shown by reactions 8 and 9.



Compound (I) is a normal radical product arising from allylic substitution. Production of compound (II), the chlorohydrin, can be reconciled by two processes. The existence of the hypochlorite (X) has already been substantiated and is assumed to give rise to the 2-chlorocyclohexoxy radical (the process of initiation is as yet undetermined). This radical could react with substrate to produce compound (II) in the manner shown in reaction 10.



Another scheme for the production of (II) involves the OCl radical. The occurrence of radical chain halogenation by chlorine monoxide produces $\cdot\text{OCl}$ (Part A) which leads to hypochlorous acid (eq. 11). Hypochlorous acid could then add to cyclohexene to give the resulting chlorohydrin (eq. 12, 13). Equilibrium 12 was shown to exist in the reaction of chlorine monoxide with saturated



substrates (Part A). The occurrence of reaction 13 was substantiated by reacting hypochlorous acid with cyclohexene in the dark at -20° . An interesting facet of the reaction of hypochlorous acid with cyclohexene in the presence of carbon tetrachloride is that besides the expected trans-2-chlorocyclohexanol, lesser amounts of (I), (III), (IV), and (V) were found in the reaction mixture. The formation of these products in reaction 13 is some further supporting evidence for equilibrium 12 which exists when hypochlorous acid is shaken in the presence of carbon tetrachloride (2). The chlorine monoxide in the organic phase reacts further with cyclohexene (as a secondary reaction) to form the products (I), (III), (IV), and (V).

If the radical process involves a kinetic order in olefin greater than one then increasing olefin concentration should result in increasing amounts of radical products. Table III shows the product distribution resulting from varied concentrations of olefin and also the effect atmospheric amount of oxygen has on the cyclohexene/chlorine monoxide reaction. In Table III, only product (I) increases as the concentration of cyclohexene becomes greater. This is in agreement with other molecule-induced reactions that involved kinetic orders in olefin that were larger than unity (29). Since the formation of (I) is retarded by the presence of oxygen, a radical inhibitor, the production of (I) may be explained by abstraction of an allylic hydrogen. Regarding the production of (II), it is a striking feature of Table III that the amount of (II) remains essentially constant regardless of the reaction conditions. This observation is not consistent with a reaction order greater than unity. This implies that product (II) does not arise via a radical process but most likely arises from the equilibrium concentration of hypochlorous acid. Since the amount of (II) is unaffected by the addition of oxygen, then it is reasonable to assume that (II) arises from an ionic reaction (eq. 13). In other words, hydrogen abstraction is not achieved by the 2-chlorocyclohexoxy radical (eq. 10). However, this does

TABLE III

Distribution of Products from the Reaction Between Cyclohexene
and Chlorine Monoxide at Various Olefin Concentrations

(-20°, dark, CCl₄ solvent)

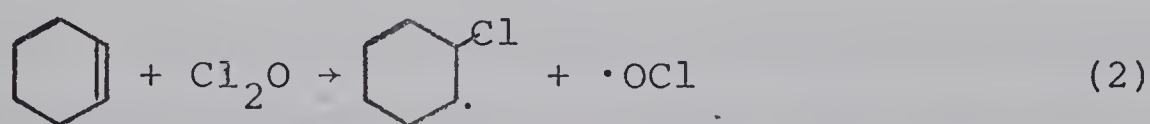
Mole excess of cyclohexene ^a	Products, mole/mole Cl ₂ O ^b			
	I	II	III	IV
3.5 degassed	0.59	0.50	0.11	0.194
10, degassed	0.79 ± 0.01	0.53 ± 0.02	0.032 ± 0.008	0.115
10, not degassed	0.38 ± 0.03	0.53 ± 0.02	0.105 ± 0.01	0.124
35, degassed	0.95 ± 0.05	0.50 ± 0.03	0.063 ± 0.006	0.092
35, not degassed	0.66 ± 0.09	0.50 ± 0.03	0.078 ± 0.026	0.105

^a Mole excess with respect to Cl₂O. Reactions were carried out in degassed ampoules or ampoules containing atmospheric amounts of oxygen (not degassed).

^b Errors are deviations from the mean of at least three experiments

not imply that radical initiation is not achieved by 2-chlorocyclohexyl hypochlorite (see reactions 4, 5 and 3).

A further anomaly with respect to kinetic order arises from the approximate enthalpies of reaction for the hypothetical interaction involving one molecule each of chlorine monoxide and cyclohexene as calculated from available bond energies (eq. 2). $D(\text{Cl}-\text{OCl})$ is the



$$\Delta H = D(\text{Cl}-\text{OCl}) + \Delta H_A = (25-26) = -1 \text{ kcal/mole}$$

dissociation energy of chlorine monoxide (Part A) and ΔH_A is the exothermicity of addition of chlorine atom to cyclohexene as used by Poutsma (29). Although the experiments give no direct information concerning the details of the initiation process, Tables I and III imply a kinetic order in olefin greater than one. On the basis of the above calculation, the minimum energy of activation for a radical-forming process is favorable when the reaction involves one molecule of each reactant. Therefore, the effect of increasing olefin concentration of radical initiation may not be kinetic, but rather an effect that results in more "interactions" which produce more radicals.

The fact that product V, arising from a free radical process (29), is found only in traces (less than 2%) can be explained on the basis of the selectivity of chlorine monoxide. As was shown earlier, the selectivity of chlorine monoxide is much like that of t-butyl hypochlorite (Part A, Tables III, IV). Therefore, it is not surprising that the abstraction of an allylic hydrogen is favored over abstraction of a "homoallylic" hydrogen. This has been shown to be true for t-butyl hypochlorite chlorinations in which the reactivity of an allylic cyclic hydrogen is about twenty-five times greater than a cyclic secondary hydrogen (27). Walling and Thaler carried out these reactions at 40°, whereas Poutsma (29) examined relative reactivities per hydrogen for abstraction by t-butoxy radical at 25° to obtain the values of: 3-cyclohexenyl : 4-cyclohexenyl : cyclohexyl : : 13.8 : 0.67 : 1.00. Poutsma gives no experimental details for the reaction. He only states that no experiments were done to determine whether these relative rates may be concentration dependent. Relative reactivities between an allylic cyclic hydrogen and a cyclic secondary hydrogen for abstraction by chlorine monoxide would be difficult to determine because of the many other products resulting from the reaction of cyclohexene with chlorine monoxide. Nevertheless, it is known that chlorine monoxide is much

more selective than chlorine (Part A) and the ratio of allylic chloride to homoallylic chloride would be expected to be much greater for chlorine monoxide chlorinations than for halogenation by molecular chlorine. An interesting feature regarding compound (V) is that it always seemed present (in small amounts) even under the conditions described in Table III. Whether or not product (V) increased with increasing olefin concentration could not be determined with any certainty (the amounts were too small to compare).

The fact that reaction 2 is energetically favorable coupled with the previous implication that the 2-chlorocyclohexoxy radical is not the abstracting species is support for radical initiation via reaction 2. However, the presence of products (IV) and (VI) lends evidence towards the formation of hypochlorite (X). In addition, the initiation involving compound (X) (reactions 4 and 5) is a bimolecular initiation which is consistent with the observation that the radical reaction is dependent upon olefin concentration. Therefore, the evidence put forth does not favor one initiating process over the other, but it has shown that cyclohexene "interacts" with chlorine monoxide to produce radicals.

EXPERIMENTAL

Materials

Phillips 66 research grade (99.94 mol %) cyclohexene was used without purification; its purity was checked by glpc. "Freon 112" (tetrachlorodifluoroethane) was distilled through an eighteen inch column containing glass helices, and the middle fraction collected. Carbon tetrachloride was distilled from phosphorous pentoxide. Cyclohexane was spectroquality reagent grade (Matheson, Coleman, and Bell) and its purity checked by glpc before use. Chlorine monoxide was prepared and analyzed as described in Part A. Concentrations of chlorine monoxide from 0.15M to 0.5M were used in the reactions. All glassware was acid washed, rinsed with ammonia then water, and dried before use.

Reaction procedure

In most reactions, two milliliters of a carbon tetrachloride solution of chlorine monoxide (0.3M) was degassed in a pyrex break seal containing a degassed sample of cyclohexene above the break seal. The sealed ampoule was then put into a covered -20° bath of glycol-water for at least fifteen minutes equilibration in the dark. The seal was broken with the aid of a teflon stirring bar contained within the ampoule, and the ampoule inverted to let the chlorine monoxide solution

run into the cyclohexene at -20° in the dark. The solution became cloudy colorless as soon as the chlorine monoxide came in contact with the cyclohexene. The ampoules were kept at -20° prior to analysis. Undegassed ampoules contained atmospheric amounts of oxygen.

Analysis

Analysis of the products from the reaction of chlorine monoxide with cyclohexene was carried out by gas chromatography (glpc) on an Aerograph Model 1520-B chromatograph utilizing the flame ionization detector and matrix programmer. All of the products, with the exception of (IV), were analyzed by elution through a 10 ft/0.125 in. polypropylene glycol (PPG) column. By use of an internal standard, "Freon 112", the absolute amounts of products (I), (II), and (III) were determined in the manner previously described in the experimental section of Part A. The peak areas were obtained from peak heights and half height peak width measurements. The injector temperature was varied from 90° to 150° and the chromatogram showed no change in distribution.

The elution of compound (IV) could only be achieved with an injector temperature of 200° or greater. The resolution of the peak due to compound (IV) was satisfactory only if the column temperature was programmed to 200° or greater. Since the PPG column is stable up to a

temperature of about 150°, the majority of product yields were obtained by using a PPG column and the yield of (IV) was obtained as an amount relative to product (III) by chromatographing the reaction mixture through a 10 ft/0.125 in. NPGS column. The peaks of (III) and (IV) were measured by cutting and weighing them out. This method was favored over measuring the peaks by half height peak widths because of the isomers of compound (IV) which resulted in overlapping peaks. Elution through both columns was about twenty minutes.

The program for analysis through the PPG column was started at 40° until cyclohexene, carbon tetrachloride, and "Freon 112" were eluted in that order. Then the oven was heated at a rate of thirty degrees per minute and held at 90° until (VII), (V), and (I) were eluted. The temperature was taken at 125° in five minutes and held at that temperature until (VIII) and (IX) were eluted in that order. Programming at six degrees per minute (just as compound (III) was being eluted) to 145° resulted in the elution of (VI) and (II) (see Table IV). The chart speed was one inch per minute. (See Figure 1).

The program for the analysis of (IV) (by an NPGS column) was initiated at a temperature of 70° and programmed at a rate such that the resolution of the peaks on the chromatogram would be satisfactory for the

TABLE IV

Relative Retention Times of the CyclohexeneReaction Mixture

Compound	Time (min)	
	PPG	NPGS
cyclohexene, CCl ₄	0	0
Freon 112	0.8	—
chlorocyclohexane	5.4	—
1-chlorocyclohexene (VII)	5.8	—
4-chlorocyclohexene (V)	6.2	5.0
3-chlorocyclohexene (I)	6.7	5.6
2-cyclohexene-1-one (VIII)	9.8	9.0
2-cyclohexene-1-ol (IX)	10.3	9.5
<u>trans</u> -1,2-dichlorocyclohexane (III)	12.2	9.8
2-chlorocyclohexanone (VI)	13.5	11.4
<u>trans</u> -2-chlorocyclohexanol (II)	14.1	11.6
2,2'-dichlorocyclohexyl ether (IV)	—	20.0

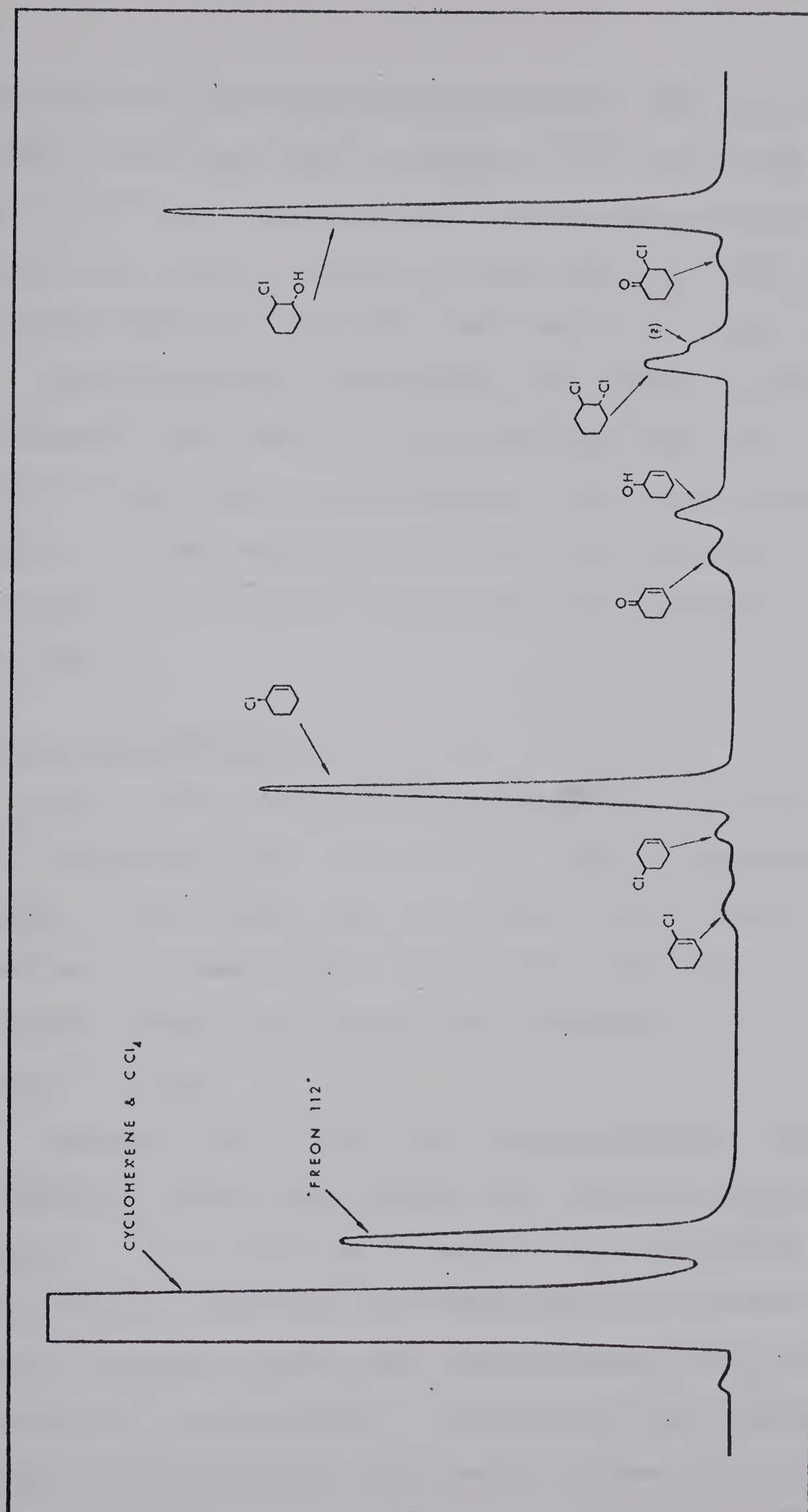


FIG. 1 Typical glpc chromatogram (10 ft./0.125 in. PPG) of products from the reaction of chlorine monoxide with cyclohexene at -20° in the dark.

comparison of the corresponding products (III) and (IV). As soon as the peak due to product (III) was eluted (at about 130°) the temperature was programmed at forty degrees per minute and held at 200° until (IV) was eluted. The chart speed was one half inch per minute. (See Fig. 2).

The reactions of cyclohexane with added amounts of cyclohexene were quenched with acidified potassium iodide solution after about twenty hours at -20° in the dark. Analysis of the reaction mixture was done by glpc utilizing the PPG column as described for previous reactions.

Product identification

Most of the products were identified by glpc and their retention times compared with those of authentic samples. The columns used for comparison of retention times were at least one of the columns mentioned previously (PPG and/or NPGS) and a 10 ft/0.125 in. SE-30 (Methyl) column.

Compounds (I), (III), and (V) were further identified by comparing their mass spectra with those of commercial samples. Due to their small amounts, the compounds were analyzed by an AEI MS12 mass spectrometer coupled to a Varian Aerograph series 1200 chromatograph fitted with a 10 ft/0.125 in. PPG column. A one microliter injection of the reaction mixture into the PPG column was sufficient

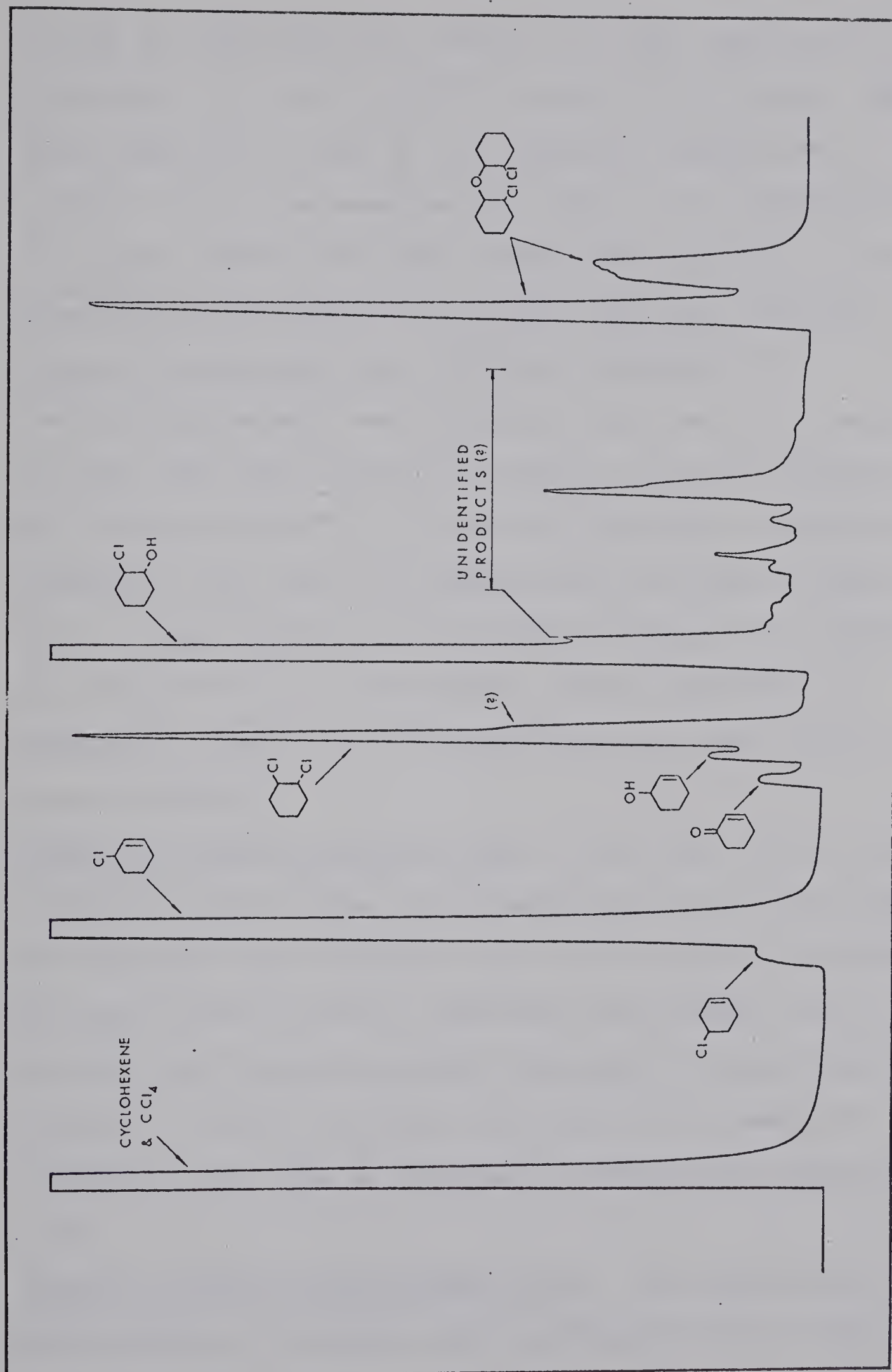


FIG. 2 Typical glpc chromatogram (10 ft. / 0.125 in. NPGS) of products from the reaction of chlorine monoxide with cyclohexene at -20° in the dark.

enough to facilitate the taking of a mass spectrum of compounds (I), (III), and (V) as they were eluted. The mass spectrum of each of the commercial samples was carried out in the same manner; that is, by chromatographing the sample through the PPG column and acquiring its mass spectrum at the instant the sample peak was recorded.

3-chlorocyclohexene (I): The peak assignment for 3-chlorocyclohexene was identical with one of the peaks arising from the reaction of chlorine with cyclohexene. The retention time on at least two different columns was identical with that of a commercially available sample of (I). A mass spectrum of the peak attributed to compound (I) showed it to be the same as a mass spectrum of a commercial sample of 3-chlorocyclohexene taken under the same conditions.

trans-2-chlorocyclohexanol (II): This peak had the same retention time as that of a commercially available sample. The compound was isolated from a "pot" reaction mixture by distillation through a spinning band column (50° at 25 mm); the infrared spectrum displayed a strong band at 3400 cm^{-1} and was identical with that of a commercial sample and the same as reported by Stevens and Grummitt (33).

trans-1,2-dichlorocyclohexane (III): The major peak from the reaction of chlorine with cyclohexene had an identical

retention time with the peak assigned as product (III). Commercially available trans-1,2-dichlorocyclohexane had the same retention time on at least two different columns as compared to the peak attributed to (III) in the reaction mixture. A mass spectrum of the peak attributed to compound (III) showed it to be identical to a mass spectrum of a commercial sample of trans-1,2-dichlorocyclohexane taken under the same conditions.

2,2'-dichlorocyclohexyl ether (IV): As a high boiling compound, this product was not noticed until a discrepancy arose in the material balance. Further investigation showed this compound to be present in quantities comparable to the dichloride (III). Ether (IV) was isolated and identified in the following manner.

At room temperature, fifteen millimoles of chlorine monoxide in carbon tetrachloride was added, with stirring, to about two hundred millimoles cyclohexene. The solution became cloudy and warmed to about forty degrees and was left stirring for at least one and a half hours. Carbon tetrachloride, excess cyclohexene, and most of product (I) were distilled under vacuum (20 mm) through a twenty centimeter vigreux column while maintaining a pot temperature not greater than sixty degrees. The residue was then chromatographed through a silica gel (28-200 mesh) column; the eluent was an equal mixture of reagent

chloroform and benzene. The ether was eluted just after the dichloride (III) which came off the column just after the solvent front. A major portion of the residue (compound II) was eluted very slowly; at least three or four liters of eluent was needed to free the column of the chlorohydrin (II). An interesting feature of the chromatography was that the column turned from blue to green to brown as the residue was chromatographed. As the ether was eluted the column was blue; then as the chlorohydrin became eluted the column turned green and then became brown in color. The ether that was eluted contained small amounts of the dichloride (II) and smaller amounts of the allylic chloride (I). The fraction containing mainly (IV) was purified by vacuum distillation by collecting the fraction that distilled at 90-95°/0.1 mm. Analysis by glpc showed the fraction to contain at least two compounds. The chromatogram showed a major sharp peak followed by a smaller broad peak in the ratio of 7:3 respectively. Since four isomers of the ether are possible, it is reasonable to assume that the purified fraction of compound (IV) contains these isomers. Anal. Calc. for $C_{12}H_{20}OCl_2$: C, 57.37; H, 7.97. Found: C, 57.24; H, 7.79. Also consistent with the formula was a mass spectrum. The exact mass by a mass spectrum was 250.0891 and a pattern of three peaks in the ratio of

9:6:1 at the parent peak was indicative of the presence of two atoms of chlorine in the molecule. The infrared spectrum of compound (IV) shows a broad ether band at 1095 cm^{-1} and no carbonyl or alcohol bands. The nmr spectrum shows two broad multiplets at 6.3τ and 8.2τ in the ratio of 1:4 respectively. This is comparable to the nmr spectrum of trans-2-chlorocyclohexanol which shows peaks at 5.65τ , 6.4τ , and 8.4τ in the ratio of 1:2:8 respectively.

4-chlorocyclohexene (V): The peak assigned to 4-chlorocyclohexene was present in chlorine/cyclohexene and iodobenzene dichloride/cyclohexene reactions. A commercial sample had an identical retention time as the assigned peak when analyzed on three different columns. A further identification of product (V) was carried out by comparison of the mass spectrum of product (V) with that of a commercial sample. The mass spectrum of a commercial sample of 4-chlorocyclohexene was taken under the same conditions as a mass spectrum of product (V). The comparison of the spectra confirmed that the peak assigned as product (V) was 4-chlorocyclohexene.

2-chlorocyclohexanone (VI): This compound was prepared by passing chlorine through an aqueous solution of cyclohexanone (Fisher Scientific Co., purified grade) and collected at reduced pressure (30 mm) at 60° (34). Its

purity was checked by glpc and the infrared spectrum showed a carbonyl band at 1720 cm^{-1} . A

2,4-dinitrophenylhydrazine derivative melted at 239° - 241° with decomposition. This prepared sample displayed a retention time equal to one of the minor peaks in the cyclohexene/chlorine monoxide reaction mixture. The same peak decreased in size when the reaction mixture was shaken with a solution of 2,4-dinitrophenylhydrazine. An infrared spectrum of the reaction mixture displayed a medium band at 1720 cm^{-1} .

1-chlorocyclohexene (VII): A peak eluted just before 4-chlorocyclohexene peak had a retention time equal to a sample of 1-chlorocyclohexene.

Other products: Two products in the reaction mixture of cyclohexene/chlorine monoxide were identified as 2-cyclohexene-1-one (VIII) and 2-cyclohexene-1-ol (IX) by comparison of retention times with commercial samples. Isolation by preparative gas chromatography was improbable because of insufficient amounts (less than 10% of all products). These peaks, (VIII) and (IX), were always present when the mixture was analyzed, although their areas varied with varied cyclohexene concentrations. The areas of these two peaks were greatest for undegassed reactions. The peaks also increased if the reaction mixture remained at room temperature for any period of

time. Therefore, the reactions were done and kept at -20° to minimize the production of (VIII) and (IX).

That cis-1,2-dichlorocyclohexane was not produced in detectable amounts in the dark reaction of chlorine monoxide with cyclohexene at -20° was shown by addition of the compound to the reaction mixture and comparing retention times. The peak attributed to the cis-dichloride was not present in the reaction mixture. This compound was prepared from trans-2-chlorocyclohexanol reacted with thionyl chloride in the presence of pyridine (33). Gas chromatography showed the reaction mixture to contain four products, two major and two minor. Preparative glpc was used to collect the first three products. An infrared spectrum of each of the products was identical with those reported for 1-chlorocyclohexene (VII), trans-, and cis-1,2-dichlorocyclohexane; eluted in that order (33). The cis:trans ratio was approximately 2:1. The dichlorides accounted for at least eighty per cent of the products of the above described reaction.

Production of chlorocyclohexane in the reaction of cyclohexene and chlorine monoxide could not be disproved since the retention time of chlorocyclohexane is close to that of 1-chlorocyclohexene (VII) and the peak attributed to VII (less than 1%) was spread out (see Table IV). However, if any chlorocyclohexane was produced it was only in traces (less than 1%).

Reduction of 2-chlorocyclohexanone with aluminum iso-propoxide affords cis- and trans-2-chlorocyclohexanol (33). The cis compound was not isolated. The mixture of cis- and trans-2-chlorocyclohexanol was analyzed by glpc and comparison of retention times of this mixture with that of the cyclohexene/chlorine monoxide reaction mixture showed the absence of cis-2-chlorocyclohexanol.

Determination of minor product quantities

The areas of the minor product (V-IX) peaks on the chromatograms were measured to obtain a rough estimate of their amounts. The areas of these minor peaks were extrapolated to mole quantities by comparison to major products whose area ratio to mole ratio was known. For example, the area of V was about a thirtieth of (I); therefore, the mole quantity of (V) was extrapolated to 3.3% of 0.79 (Table II). Each of the other minor compounds was compared to a major product of similar structure and/or boiling point. Compounds (V) and (VII) were compared to (I) while the amount of (VI) was measured relative to product (II). Both products, (I) and (II), were used to determine the amounts of (VIII) and (IX). In this manner an estimate of the amounts of each of the minor products was obtained.

The amount of chlorine present in the unidentified products is reported as a range, on the assumption that

these products contain at least one or two chlorine atoms per molecule of product (see Table II). One of the unknown compounds was measured by comparison to trans-1,2-dichlorocyclohexane because of a similar retention time and hence a similar boiling point with that of the dichloride. The rest of the unknown compounds (at least five) were measured relative to the ether (IV) because of retention times similar to that of the ether.

Hypochlorous acid reaction

The reaction of hypochlorous acid (prepared as in Part A) with cyclohexene was carried out in a degassed ampoule with a ten fold excess of cyclohexene in carbon tetrachloride and reacted via a break seal as described earlier. The ampoules were put in a -20° bath and shaken vigorously during the course of reaction. After two minutes, 25% of the hypochlorous acid still remained and after five minutes the reaction was at least 95% complete. After ten minutes of shaking at -20° in the dark, the reaction mixture showed less than one per cent titer (greater than 99% reaction). Analysis of the mixture by glpc showed the presence of some products present in the cyclohexene/chlorine monoxide reaction. The main product was the chlorohydrin (II). Compounds (III) and (IV) were present in equal amounts (about 25%

of II) and compounds (I) and (V) were also present; together they made up about 10% of the total. The ratio of (I):(V) was about 2:1.

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